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(54) Reduction of residual monomers in superabsorbent polymers.

(57) Techniques for obtaining superabsorbent polymers having less than 10 parts per million residual monomer particularly (meth)acrylic acid monomers, are disclosed. These techniques involve the use of combination products including surfactants and vinyl addition compounds. The surfactant can be any surfactant having an HLB ranging from 3 - 40 and the vinyl addition compound can be any material capable of reacting with vinylic double bonds to obtain products which cannot polymerize by free radical polymerization. The preferred surfactants also reduce the surface tension of water to within a range of from 15 to 50 dynes per centimeter.

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The formation of the so called "superabsorbent" polymers requires polymerization of various types of normally water soluble monomers, but often water insoluble comonomers in conjunction therewith, in the presence of cross-linking agents. The cross- linking agents may be added during polymerization or after polymerization. These superabsorbent polymers are slightly cross-linked, water-insoluble, hydrogel polymers, and, when dried and essentially free of water have an incredible capacity to absorb water.

As a result, these superabsorbent polymer materials are quite useful as adjuncts in water absorbing structures and articles such as baby diapers, incontinence control products, sanitary napkins, and the like.

Because these superabsorbent materials may be in close proximity to human skin, it is desirable to remove any low molecular weight compounds or components from the superabsorbent cross-linked polymeric materials, when these low molecular weight compounds may cause skin irritation or pose any other potential health threat.

These low molecular weight materials can include oligomers of water soluble polymers, which did not become cross-linked, but most importantly are the initial monomers which are used to form the superabsorbent lightly cross linked polymeric structures.

It is an object of this invention to reduce residual monomer content of both high molecular weight (i.e. above 10,000,000 Daltons) water soluble and slightly cross-linked, water insoluble, high molecular weight polymers. It is particularly an object to reduce total residual monomer content to concentrations below 50 parts per million based on dry polymer.

It is another object of this invention to reduce, from a superabsorbent lightly cross-linked water insoluble polymer, the monomer content contained therein to concentrations below at least 50 parts per million, based again upon dry weight of the polymer.

It is yet another object of this invention to reduce (meth)acrylic acid monomer content within superabsorbent lightly cross-linked water insoluble polymers, which polymers have been manufactured using (meth)acrylic acid or its salts. As used herein, the term (meth)acrylic acid is meant to include acrylic acid, methacrylic acid, any mixture of acrylic acid and methacrylic acid, and any water soluble salts thereof.

Finally, it is an object of this invention to reduce to levels below 25 parts per million, and preferably below about 10 parts per million, based on dry polymer weight, the amount of acrylic acid, methacrylic acid, or salts thereof, which are contained in superabsorbent lightly cross-linked water insoluble polymers which polymers are manufactured using acrylic acid, methacrylic acid, any combination thereof, and/or any combination of free acid or salts thereof.

High molecular weight water soluble and water insoluble polymers which are manufactured from (meth)acrylic acid, i.e. acrylic acid, methacrylic acid, mixtures thereof or salts thereof, have been used in the past as flocculants, coagulants; and, when cross-linked with any number of cross-linking agents, form water-insoluble, hydrogel-forming polymers capable of absorbing large quantities of aqueous fluids, such as water or aqueous body wastes. These superabsorbents are further capable of retaining these absorbed aqueous fluids under moderate temperatures and pressures. The absorption characteristics of these hydrogel-forming polymers make them especially useful for incorporation into absorbent articles such as disposable diapers, incontinence products, sanitary napkins, and the like. (See Harper, et. al., U.S. 3,669,103 and Harmon, U.S. 3,670,731 both of which are incorporated herein by reference).

These hydrogel-forming superabsorbent materials may be made from water absorbing starch resins, which are made by graft polymerizing unsaturated monomers, such as acrylic acid and/or methacrylic acid or its salts, onto various polysaccharides such as starch, cellulose, dextrans, and the like. Sometimes this grafting process is followed by cross-linking the resulting grafted polymers. Exemplary of cross-linked grafted starch resins is Masuda, et. al. U.S. 4,076,663, which is incorporated herein by reference.

These water-insoluble, lightly cross-linked hydrogel-forming materials can also comprise only cross-linked polymerized unsaturated monomers. The synthetic hydrogels contain no starch, no cellulose, no dextran, or any other polysaccharide onto which the polymer is grafted, but instead are synthesized from monomers such as acrylic acid, methacrylic acid, acrylamide, maleic acid, maleic anhydride, vinyl sulfonate, and methyl and ethyl acrylate, and the like. Exemplary of such materials are those materials described in:

Brandt, et. al., U.S. 4,654,039
Tsubakimoto, et. al., U.S. 4,286,082
Westerman, U.S. 4,062,817
Obayashi, U.S. 4,340,706
Yuki, U.S. 4,654,393

Each of which is incorporated herein by reference.

Additionally, all of the patents cited and listed in each of the above patent references are also herein incorporated herein by reference.

Basically, the above patents, excluding the patents teaching carbohydrat grafted materials, teach the use

of acrylic acid or methacrylic acid, or their water soluble salts, or admixtures thereof with other monomers, to form high molecular weight lightly cross-linked water insoluble gel forming polymers which, when dried, have remarkable abilities to absorb many times their own weight in water or body fluids containing water.

There are many variations for manufacturing these high molecular weight polymers, such variations including polymerizing (meth)acrylic acid either as the free acid(s) or as neutralized salts, i.e., sodium acrylate, or performing the polymerization with anything from pure acrylic acid (unneutralized) to partially neutralized monomer acids, i.e. in excess of 75 mole percent neutralized with sodium hydroxide (or other alkali, such as sodium carbonate) neutralized salts of acrylic acid. These monomers may be added to water, either to form a solution or an inverse water-in-oil emulsion, and are then polymerized by the addition of polymer initiators, such as the free radical initiators exemplified in U.S. 4,654,039. These free radical initiators can include but are not necessarily limited to peroxygen compounds such as sodium, potassium, and ammonium persulfates, caprylyl peroxide, benzoyl peroxide, hydrogen peroxide, cumene hydroperoxides, tertiary butyl diperphthalate, tertiary butyl perbenzoate, sodium peracetate, sodium percarbonate, and the like. Other free radical initiators can include the conventional redox initiator system which include some form of peroxygen compounds, such as those listed above, in combination with reducing agents, such as sodium bisulfite, L-ascorbic acid, various ferrous ion salts, and the like. Organic free radical pre-cursors, such as the VAZO® catalysts, may also be used. Login, et. al., U.S. 4,473,689, incorporated herein by reference, teaches the use of certain minimum polymerization initiator concentrations in the context of preparing water-soluble polymer materials.

The acrylic acid, methacrylic acid, or partially neutralized salts thereof, or mixtures thereof are generally made up in water solution, or in a water-in-oil emulsion. When a water solution is polymerized, the solution can contain as little as about from 5 - 15 weight percent of total monomer and as much as from 40 - 95 weight percent total monomer, or monomer mix. To this aqueous solution is added a cross-linking agent, which cross-linking agent generally is added in the amount from about 0.001 mole percent to 5 mole percent based on total moles of monomer present in the aqueous mixture. Preferably the cross linking agent is contained in the aqueous mixture from about 0.01 mole percent to about 3 mole percent of total monomer present in aqueous mixture. To this mixture, the free radical initiator is added and polymerization is initiated and proceeds normally. Polymerization can proceed in an aqueous emulsion or in an aqueous gel, or it can proceed in an inverse solution, i.e. a water-in-oil dispersion polymerization. In some cases, particularly the inverse suspension technique for making superabsorbent polymer beads, the cross-linking agent is added after polymerization has been nearly or totally completed.

As the polymerization reaction continues, and nears completion, very high conversion of acrylic acid or methacrylic acid, or admixtures thereof, either as the free acid or partially neutralized water soluble salts, to the hydrogel is achieved. The characterization of the hydrogel is carefully controlled by monomer concentration, type and ratio of monomers, type and amount of cross-linking agents, type and amount of initiators used, polymerization times and temperatures, the nature of the reaction medium, and procedures used for polymer recovery and/or drying. The hydrogel polymer, depending on these many variables can have any particular combination of gel volume, gel strength, extractable polymer content, and the like. These characteristics are spelled out in U.S. 4,654,039, and the superabsorbents of our invention have these desired parameters.

Although U.S. 4,654,039 teaches the use of polymerization of free acid monomers, other patents such as U.S. 4,286,082, and U.S. 4,340,706, both of which are incorporated herein by reference, prefer to use mixtures of the free acid monomers and their water soluble salts for the synthesis of the hydrogel forming polymers.

Also, U.S. 4,340,406, and U.S. 4,506,052, also incorporated herein by reference, teach polymerization by inverse suspension to form superabsorbing hydrogel polymers. Polymers made by this inverse emulsion or inverse suspension technique are also included within the scope of this invention.

Irrespective of any of the techniques above, which are used to manufacture the hydrogel polymers having superabsorbing characteristics, these polymers heretofore have contained residual monomers, i.e. residual acrylic acid or (meth)acrylic acid monomers, or water soluble salts thereof. The concentrations of these residual (meth)acrylic acid monomers could provide for skin irritation to sensitive persons in contact with the products containing the same. Other attempts have been made to remove these monomers to low concentration values, thereby decreasing any potential health or safety hazard due to the content or residual monomer. For example, U.S. 4,766,173, Bailey, et. al., covers a method of reducing residual acrylic acid present in water-insoluble polyacrylic acid, water absorbent, gel polymers by treating the polymers with amino chosen from the group consisting of cysteine or lysine. The cysteine and lysine used was ratioed to the acrylic acid present in the superabs rbent materials.

In like fashion Chm lir, U.S. 4,929,717, teaches a method of preparing homopolymers or copolymers that are water solubl or that swell up in water and have low residual monom r content. The polymers are treated

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with a compound that can react and add across the monomer double bond. These compounds are taught to include ammonia, ammonia salts, alkyl amines or their salts, hydroxylamines or their salts, hydrogen halides, acetyl acetonates, malonates that contain active hydrogen atoms, bromosuccinimide, pyridinium bromide, dioxane perbromide, or any compound which contains bromine or releases bromine which bromine then add across the double bond.

Other vinyl addition compounds, or vinyl reactive compounds include permanganate, bichromate, chromate, selenium dioxide, ozone, or other compounds which may oxidize the vinylic double bond, or with compounds such as alkali sulfites, ammonium sulfites, alkali or ammonium hydrogen sulfites or disulfites, thio compounds containing sulphur. Again, these compounds can add across or reacted with the double bond. These reaction are allowed to occur within the polymer gel and permit the polymer gel to be dried at elevated temperatures, thereby releasing a polymer gel which has lower content of these monomers. Monomer residual content is lowered from about 500 - 1000 ppm to about 100 - 200 ppm, based on polymer.

Both U.S. 4,766,173 and U.S. 4,929,717 are incorporated herein by reference.

Finally, the following patents are cited in U.S. 4,929,717, which patent teach various techniques for treating polymers or polymer gels so as to remove unreacted monomer or convert unreacted monomer to other components and compounds, thereby lowering the residual content of monomer contained in the polymer materials.

U.S. 2,960,486
U.S. 4,132,844
U.S. 3,755,280
U.S. 3,780,006
U.S. 4,529,753
U.S. 4,414,063
U.S. 4,585,808
U.S. 4,375,529

Each of these U.S. patents are incorporated herein by reference.

In addition, other patents or patent applications are also cited in the '717 patent, which patent applications and patents were filed in other countries and includes the following :

German Patent Appln. 1,070,377
Japanese Patent No. 53/51289
Japanese Patent No. 50/136382
Japanese Patent No. 56/103207
Japanese Patent No. 55/151015
European Patent No. 0175554
German Patent No. 2919096
European Patent No. 002860
CS Patent 210100
Great Britain Patent No. 2113694

A careful review of each of these references shows that these are numerous ways that the artisan has attempted to solve the problem of removing residual monomer from high molecular weight polymers and superabsorbents. These techniques include reaction with sodium sulfite followed by drying, extraction with methanol or mixtures of methanol and water followed by drying, treating polymer gels with aqueous solution of sodium bisulfite and with solid alkali sulfite, even sulphur dioxide gas; the addition of tertiary butyl hydroperoxide and sodium metabisulfite, the addition of ethanol amines, the use of steam distillation, isotropic distillation, high energy radiation, and catalytic hydration.

In spite of the many attempts to remove residual monomers, particularly acrylic acid, methacrylic acid, or salts thereof, from these polymers and lightly cross-linked superabsorbent polymer gels, the art has not regularly or successfully taught a consistent and reliable removal of these monomers to levels below 50 parts per million, based on dry polymer weight. These is no art which teaches a removal below 10 parts per million (based on dry polymer) of acrylic acid, acrylic acid salts, methacrylic acid, methacrylic salts, or mixtures thereof.

We have invented a process for decreasing the residual (meth)acrylic acid monomer content of water soluble and water insoluble polymers to level below about 10 parts per million based on dry polymer, which process comprises adding to the polym r, aft r polymerization, aqueous solutions containing a combination of a surfactant and a chemical compound capable of adding across or reacting with the vinylic carbon carbon double bond.

Our combination treatment agent n rmally contains from 50 to 0.l weight percent of a surfactant or mixture of surfactants and from 50 to 99.9 weight percent of a vinylic addition compound, which is any chemical compound capable of adding across or otherwise reacting with the vinylic carbon carbon double bond to form another chemical component which is not capable of being polymerized by free radical initiation.

Our combination of ingredients is normally added to the polymerized mixture, either when the mixture is in a water solution, a water gel, a water-in-oil inverse suspension, or any other form of water containing the polymer formed by the reaction of acrylic acid, methacrylic acid, neutralized or partially, but are not limited to, neutralized (meth)acrylic acid, or water solutions containing these vinylic carboxylic monomers in conjunction with other water soluble monomers. The other water soluble monomers can include, but are not limited to, at least one of some other unsaturated carboxylic acids and/or carboxylic acid and anhydride monomers, such as ethacrylic acid, alpha-cyano acrylic acid, beta-methyl- acrylic acid, alpha phenyl acrylic acid, beta-acryloxy propionic acid, sorbic acid, itaconic acid, glutaconic acid, maleic acid, fumaric acid, maleic anhydride, fumaric anhydride, and the like. These vinylic monomers can also include monomers which contain sulfonic acid functionality and can include, but are not limited to, the aliphatic or aromatic vinyl sulfonic acids, such as vinyl sulfonic acids, allyl sulfonic acids, vinyltoluenesulfonic acid, styrene sulfonic acid, acrylic and methacrylic sulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, 2-acrylamido-2-methyl propane sulfonic acid, and the like.

Additionally, neutral vinylic monomers can include, but are not necessarily limited to, acrylamide, methacrylamide, N-methyl acrylamide, ethylacrylate, methylacrylate, and other carboxylic acid or sulfonic acid ester containing monomers, hydroxyl group containing monomers, amide group containing monomers, amino group containing monomers, nitryl group containing monomers, and quaternary ammonium salt group containing monomers. Various monomers are spelled out in greater detail in Masuda, et. al., U.S. 4,076,663, and Westerman, U.S. 4,062,817, each earlier incorporated herein by reference.

Primarily, however, our invention is aimed at solving a problem of removing residual acrylic acid, methacrylic acid, or salts thereof contained in high molecular weight polymer gels, particularly the lightly cross-linked water insoluble high molecular weight hydrogel-forming superabsorbent polymer compositions useful to absorb large quantities of water or body fluids containing water.

Our process decreases the residual (meth)acrylic acid monomer content of these superabsorbent polymers to levels below about 50 parts per million, and preferably below about 10 parts per million (on the basis of dry polymer), and comprises the addition, preferably by spraying (but also by immersion), of an aqueous solution containing our combination products of surfactant and vinylic addition compounds onto a chopped up polymer gel or pre-formed polymer beads, which chopped gel or beads can contain anywhere from about 5 to about 95 weight percent polymer. The combination product contains the surfactant and the chemical vinylic addition compounds described above. This combination product, which as earlier stated contains from 50 to 0.1 weight percent surfactant and from 50 to 99.9 weight percent of a chemical vinylic addition compound is itself contained in an aqueous solution or suspension at concentrations ranging from about 0.0l weight percent to about 25 weight percent, preferably from about 0.05 weight percent to about 10 weight percent, and most preferably from about 0.25 weight percent to about 5 weight percent of the total of the combination products. The combination product can contain both surfactant and vinyl addition compound in weight ratios of from 50:50 to about 0.1 to 99.9.

The combination product is a combination of a surfactant or a mixture of surfactants and a chemical vinylic addition compound, or mixtures of these types of compounds, in the above listed weight ratios. The surfactant may be any surfactant which has an Hydrophilic-Lipophilic Balance (HLB) ranging from about 3 to about 40, preferably a surfactant ranging in HLB from about 8 to about 40, and most preferably a surfactant which has an HLB ranging from about 12 to about 40. The surfactant also should be capable, when added to pure distilled water at a concentration of at least 100 - 1000 parts per million, of lowering the surface tension of this water, in contact with air, from about 72.3 dynes/cm to a surface tension ranging from about 15 to about 50 dynes/cm, preferably from about 20 to about 40 dynes/cm, and most preferably from about 20 to about 35 dynes/cm, (all surface tension values at standard temperatures and pressures).

The most preferred surfactants are the methoxy terminated ethylene oxide, adducts of siloxanes, 4 - 24 mole ethylene oxide adducts of C_{12}-C_{14} fatty alcohols, or the alkali metal salts of fatty acids sulfates, which fatty acid sulfates contain from 10-30 carbon atoms, and preferably from 10-24 carbon atoms or the ethylene oxide/propylene oxide adducts of glycol, or glycerine, or mixtures thereof. The surfactant may also be ethylene oxide adducts of phenols or substituted phenols or oligomers of ethylene oxides and/or propylene oxides.

Our surfactants may be fatty acid materials, or salts of fatty acids, which fatty acids contain from about 10 to ab ut 30 carb n atoms, preferably from about 12 to about 24 carbon atoms, th y are preferably alkali metal salts of fatty acids containing from l0 to 30 carbon atoms, most preferably between about 12 - 24 carbon atoms. The alkali metal salts preferred are sodium or potassium salts of stearic acid and/or lauric acid.

The surfactants in our combination product may be single surfactant materials or they may be mixtures of surfactants, such as any mixture of those specific surfactant listed above, or others.

The chemical vinyl addition compound materials are materials capable of adding across or reacting with a vinylic doubl bond so as to form reaction product(s) which is incapable of vinylic polymerization by free radical

initiation. Such chemical vinylic addition compounds include, but are not necessarily limited to, alkali metal salts of sulphites, alkali metal salts of bisulphites, or mixtures thereof. They may also include alkyl or aryl, or substituted alkyl or aryl sulfinic acids, or water soluble salts thereof, or mixtures thereof, and also include alkali metal salts of hypophosphites, sulfur containing amino acids such as cysteine, lysine or water soluble salts thereof, various thio sulfate derivatives or their combinations, bichromates, chromates, selenium dioxides or ozone. In addition, bromosuccinimide, pyridinium bromides, dioxane perbromides, hydroxylamine or hydroxylamine salts, and the like, also are within this class of compounds. These compounds may be used singly, in admixture with one another, or in admixture with salts of oxidizing anions, such as persulfates, peroxide, and the like.

These vinylic addition compounds are preferably chosen from the group consisting of alkali metal bisulfite salts, such as potassium bisulfite, sodium bisulfite, and the like, alkyl or aryl, or substituted alkyl or aryl sulfinic acids, or water soluble salts thereof, sodium or potassium salts of hypophosphites, sodium or potassium salts of cysteine and/or lysine or the free amino acids, cysteine and lysine, or any admixture of the above.

When practicing my process for obtaining a superabsorbent polymer containing residual (meth)acrylic acid monomer at levels below about 50 and preferably below about 10 parts per million (based on dry polymer), I initiate polymerization of the (meth)acrylic acid, or partially or completely neutralized solutions thereof, with any of the number of free radical initiators, of like initiators, listed above. The polymerizing solutions contain any of a number of different cross-linking agents, but my preferable cross-linking agents are chosen from the group consisting of N,N'-methylenebisacrylamide, trimethylol propane triacrylate, triallylamine, diallylamine, and the triacrylic acid esters of ethylene glycol, trimethylol propane, glycerine or other polyoxy ethlene glycols, or any mixtures thereof. The polymerization is continued in solution or in a water-in-oil dispersion or emulsion.

These various end/products gels normally contained anywhere from about 200 to about 1,500 parts per million unreacted acrylic acid, methacrylic acid, or salts thereof. These gels are then chopped into small particles in preparation for a drying step. The chopped gel particles range in size (average diameter) from about 50 microns to about 50,000 microns, or higher. If the inverse suspension process gel is used, the particle size ranges from 10 microns to 5,000 microns. These bead materials are then separated by settling and filtering from the oil continous phase. There is no need to chop these beads before drying.

Immediately before a drying step, I spray or otherwise contact the chopped gel or beads with an aqueous solution of my combination product while mixing to insure best coverage of the combination product solution sprayed onto the particle with the chopped gel particles. My aqueous sprays can contain the surfactants and vinyl addition compounds described above in the ratios described above. The spray solutions contain both the surfactant and the vinyl addition compounds at those concentrations described above. Primarily, the vinyl addition compounds are added in such a manner in the spray solution so as to be present on at least a mole per mole basis or above. Preferably, this treatment level is at least 2 moles vinyl addition per mole residual monomer and is preferably at least 5 moles vinyl addition compound per mole of residual monomer, especially when treating the chopped gels.

The spray solutions containing my combination products are normally made up in distilled or deionized water, but may also be made up in softened water. Hardness ions, such as calcium and magnesium, should be avoided. The aqueous solutions normally contain from 0.05 to 25 weight percent of my vinyl addition compound, preferably from 0.25 to 10 weight percent of this vinyl addition compound and from 0.01 to 5 weight percent of surfactant, preferably from 0.05 to 1.5 weight percent surfactant. Most preferably, the spray solutions contain from 0.05 to 0.5 weight percent surfactant. Although my combination product is preferably a material which forms aqueous solutions, these products may also form dispersions having cloudy appearance, particularly when the surfactant is a material having a lower HLB, for example an HLB below about 8. The aqueous spray containing the combination product is added to the gel particle so as to provide from about 0.05 to 10 weight percent of the combination product solution to the gel (as calculated on the basis of wet gel polymer). The treated gel is then mixed and dried. Drying is normally from 180° F to 400° F, preferably from 210° F to 375° F, and most preferably from 210° to about 350° F.

Alternatively, I can chop the gel into its particulate form and dry it at temperatures ranging from about 180° F to about 400° F and then spray my combination product onto the dried polymer. This wetted dried polymer containing my combination products is then mixed and dried for a period of from about 1 minute to about 2 hours. Drying temperatures range from about 180° F to 400° F, preferably 210° F to 375° F to achiev similar reduced residual monomer results.

Although it is convenient in the process to spray an aqueous solution preferably formed by the use of deionized or distilled water, which aqueous solution contains most preferably from 0.10 to 10 weight perc nt of sodium bisulfit , sodium hypophosphinic acid, alkyl or aryl, or substituted alkyl or aryl sulfinic acids or its sodium or potassium salts, or mixtures thereof, in th pr sence of surfactants chosen from the group consisting of sodium or potassium lauryl sulfates, ethoxylated polydimethyl siloxane/methoxy capped, 6-12 mole ethoxylates

of C_{12} - C_{14} fatty alcohols, glycerine initiated ethylene oxide-propylene oxide adducts, sodium or potassium stearates, or surfactant mixtures thereof, where the surfactant is present in the spray solution anywhere from about 0.05 to about l.5 weight percent.

After the chopped gel or polymer beads has been sprayed with our aqueous solution (or dispersion) of the combination product containing the surfactant and the vinyl addition compound, the spray treated and particulated polymer gel is then mixed for from 10 seconds to 2 hours at from 70° F to about 200° F and is then dried at temperatures ranging from about 180° F to 400° F, preferably from 210° F to 375° F, and most preferably from 210° F to 350° F, for a period ranging from about 2 minutes to about 2 hours, preferably the drying step takes from 5 minutes to 30 minutes.

The dried materials consistently analyze as containing considerably reduced concentrations of residual acrylic acid, methacrylic acid, or salts thereof, such residual (meth)acrylic acid concentrations often being below 50 parts per million, based on dry polymer weight, most preferably and most frequently below about 10 parts per million acrylic acid monomer based on dry polymer weight.

Although the above descriptions are primarily based on polymer gels containing from 5 to 60 weight percent polymer, and preferably from about 30 - 50% polymer, similar good results are obtained when our combination product is added to inverse suspension produced superabsorbents, either dried or as the final emulsion before drying.

To further exemplify my invention, the following examples are given:

EXAMPLES

Treatment of laboratory synthesized cross-linked polyacrylic acid superabsorbent wet gel with a solution containing 2 weight percent sodium bisulfite and 0.1 weight percent of a surfactant, using different treatment techniques outlined below, reduce the residual acrylic acid significantly lower than the levels of acrylic acid obtainable when sodium bisulfite was used alone and in the absence of the surfactant. Five different surfactants were tested in combination with sodium bisulfite, which surfactants included Silwet L-7607, potassium stearate, sodium lauryl sulfate, 6-8 mole ethoxylated C_{12} - C_{14} alcohols, glycerine initiated EO/PO adducts, and mixtures thereof.

The experiments were performed on several laboratory generated wet gels (about 40 weight % polymer) containing primarily a partially neutralized sodium acrylate in admixture with acrylic acid, a multi unsaturated cross-linker, and a free radical initiator, and with a wet gel (also about 40 weight % polymer) made in an industrial process. Further work was done with a dried powder obtained from the industrial process and with a dry material obtained from a water-in-oil dispersion product.

Experiments are outlined below in the following tables:

TABLE 1

SAMPLE 3222-	* %SBS	%SBS** SOL	%POTASSIUM*** STEARATE	LAB WET GEL (G)	RESIDUAL AA (PPM)
192N (control)	--	--	--	113	730
192A	1	10	0.1	250	110
192B	2	10	0.1	250	19
192C	3	10	0.1	250	19
192D	4	10	0.1	250	11
192E	5	10	0.1	250	13
192F	6	10	0.1	250	12
192G	--	--	0.1	250	396
192H	1	10	--	250	84
192I	2	10	--	250	53
192J	3	10	--	250	27
192K	4	10	--	250	11
192L	5	10	--	250	11
192M	6	10	--	250	9

* weight % sodium bisulfite (based on wet gel polymer)
** weight % sodium bisulfite in the spray solution
*** weight % based on wet gel polymer
AA = Acrylic Acid

In table 1, results are obtained by treating laboratory generated wet gel containing approximately 40 weight percent of a partially neutralized, slightly cross-linked sodium acrylate/acrylic acid superabsorbent polymer, which gel contained less than 3 weight percent (based on polymer) crosse linker, and which gel had been initiated with free radical initiators. The reaction had been run at elevated temperatures, essentially adiabotically, until completed. The gel formed was chopped into particles and aqueous solutions containing the indicated amounts of sodium bisulfite and potassium stearate were sprayed onto the chopped gels using a laboratory atomizer. Total weight of the sodium bisulfite and potassium stearate are set forth in the table, as is the amount of wet gel treated and the residual acrylic acid determined.

The residual acrylic acid was determined by a liquid chromatography method which took a 2 gram sample of final treated polymer, added this sample to water solvents to a total of 400 grams dilution, extracted this diluted sample with 0.02 molar sulfuric acid, and added an aliquot of this extraction solution to a dual column liquid chromatograph. Various chromotographic packings can be used. The technique was demonstrated to be capabl of determining a lower limit of quantification equal to about 1.0 parts per million acrylic acid (based on dry polymer), and had an estimated lower limit of detection of approximat ly 0.3 parts per million acrylic acid (BODP). The percent relative standard deviation for this analytical technique is approximately 6 p rcent at 8 degrees of freedom, as determined on samples having 13 parts per million residual acrylic acid based on dry polymer. All residual monomer concentrations reported ar calculated based on dry polymer, i.e. BODP.

In table 1, the 192N control was simply an analysis of the laboratory generated wet gel, which was determined to contain 730 parts per million acrylic acid monomer (BODP). In the presence of sodium bisulfite and potassium stearate, this acrylic acid residual was lowered to approximately 110 parts per million when the treatment solution contained only 1 weight percent sodium bisulfite. However, when the treatment solution contained from 2 to 6 percent sodium bisulfite monomer, residuals ranging from approximately 11 to 19 parts per million (BODP) were detected.

This result can be compared later in the same table with the addition of the same amount of sodium bisulfite in the absence of this very low amount of surfactant. As can be seen, in the absence of surfactant, these lower monomer levels are not obtained until sodium bisulfite solutions are added at concentrations ranging from 4 to 6 percent. Therefore, the presence of the surfactant at 2 and 3 percent sodium bisulfite was instrumental in decreasing the amount of residual acrylic acid.

TABLE II

SAMPLE 3222-	%SB	%SBS SOL	SURFACTANT 0.1 %	D H_2O (G)	LAB WET GEL (G)	RESIDUAL AA (PPM)
187G (control)	--	--	--	45	250	818
187A	2	10	Sodium lauryl sulfate	45	250	57
187B	2	10	Silwet L-7607 (all EO methoxy terminated siloxane)	45	250	28
187C	2	10	Surf. EO-ALC (6 - 8 Mole ethoxylated C_{12}-C_{14} alcohol)	45	250	81
187D	2	10	Voranol 4701 (glycerin initiated EO/PO)	45	250	102
187E	2	10	Potassium Stearate	45	250	157
187F	2	10	--	45	250	264
187H	--	--	Sodium lauryl sulfate	45	250	734
187I	--	--	Silwet L-7607	45	250	958
187J	--	--	Surfactant EO-ALC	45	250	1026
187K	--	--	Voranol 4701	45	250	963
187L	--	--	Potassium stearate	45	250	903
187M	2	10	Surfactant EO-ALC	45	250	76

In Table II, further results are provided with additional experiments. In this case, the 187G control was a material obtained by simply spraying with water alone the laboratory wet gel. As can be seen, this base wet gel contained approximately 818 parts per million acrylic acid. By adding sodium bisulfite and the various listed surfactants at a concentration of .01 weight percent surfactant (based on wet gel polymer weight) and 2 weight percent sodium bisulfite (based on wet gel polymer weight) considerably lower residual acrylic acid is obtained than available with just treatment with sodium bisulfite alone, or with any of the surfactants alone. In the presence of the combination of sodium bisulfite and any of five different surfactants, the residual acrylic acid found after treatment is far less than any amount of residual acrylic acid found in the blank, with treatment only with SBS (sodium bisulfite) or with treatment with only the surfactants. The wet gel treated was a day old, DI water was used to dissolve the sodium bisulfite and the surfactants.

This solution was sprayed with an atomizer onto the wet gel. Attention is also brought to example 3222-187C and 3222-187M, which are duplicates and show very reasonable reproduction of data. Table II data was generated on day old gel at room temperatures (approximately 70 - 74° F).

TABLE III

SAMPLE 3324-	%SBS	%SBS SOL	SURFACTANT 0.1 %	DI H_2O(G)	LAB WET GEL (G)	RESIDUAL AA (PPM)
1G (control)	--	--	--	22.5	125	604
1A	2	10	Sodium lauryl sulfate	45	250	7.8
1B	2	10	Silwet L-7607	45	250	2.9
1C	2	10	Surfaetant EO-ALC	45	250	6.9
1D	2	10	Voranol 4701	45	250	8.1
1E	2	10	Potassium stearate	45	250	23
1F	2	10	--	45	250	70
1H	--	--	Sodium lauryl sulfate	45	250	622
1I	--	--	Silwet L-7607	45	250	712
1J	--	--	Surfactant EO-ALC	45	250	950
1K	--	--	Voranol 4701 (HLB - 3)	45	250	882
1L	--	--	Potassium stearate	45	250	978
1M	2	10	Surfactant EO-ALC	45	250	15

In Table III above, sodium bisulfite and various surfactants were again used, this time with a fresh gel obtained by same day polymerization. Th results were also obtained from same day analysis. Sodium bisulfite was dissolved initially in the DI water followed by addition of the indicated surfactant. Although th re was no particular benefit to this sequence of making the combination, the solutions obtained by this sequence appeared

to provide better clarity, therefore better solutions and are thought to provide preferred results. As can be seen the Table III control, again using sprayed water alone, indicated a residual acrylic acid of approximately 604 parts per million. Treatment at 150° F throughout Table III indicated an ability using the combination of sodium bisulfite and the listed surfactants to obtain residual acrylic acid values consistently below 10 parts per million.

Again, as before, merely treating with sodium bisulfite or the surfactants alone (absent the vinyl addition compounds) did not provide nearly the same benefit as observed in the combination treatment.

TABLE IV

SAMPLE 3222-	%SBS	%SBS SOL	SURFACTANT 0.11 %	COMMERCIAL DRY POWDER (G)	RESIDUAL AA (PPM)
Control	--	--	--	--	300
170A	1.15	1.1	--	500	14
170B	1.15	1.1	Sodium lauryl sulfate	500	16
170C	1.15	1.1	Silwet L-7607	500	22
170D	1.15	1.1	Surfactant EO-ALC	500	16
170E	1.15	1.1	Voranol 4701	500	26
170F	1.15	1.1	Potassium stearate	500	30

Table IV present the results obtained when a dried powder obtained from the drying of commercial superabsorbent gels was treated with the sodium bisulfite alone and in combination with the surfactants. At the SBS treatment levels, which levels appear to be very high relative to residual monomer level (approximately 300 parts per million based on dry polymer), little difference was observed in the presence or absence of surfactant. However, it was believed that when using lower sodium bisulfite levels, an improvement would be observed in the presence of the surfactants. In an attempt to demonstrate this, the data in Table V was generated.

TABLE V

SAMPLE 3222-	%SBS	%SBS SOL	SURFACTANT 0.11 %	DI H_2O(G)	INVERSE SUSPENSION DRY POWDER (G)	RESIDUAL AA (PPM)
196A (control)	--	--	--	266	250	57
196B	0.58	0.54	--	133	250	8.7
196C	0.58	0.54	Sodium lauryl sulfate	133	250	7.4
196D	0.58	0.54	SURF. EO-ALC	133	250	9.9
196E	--	--	Sodium lauryl sulfate	133	250	43
196F	--	--	SURF. EO-ALC	133	250	41

In Table V, a control using dry powder superabsorbent obtained from water-in-oil dispersion (inverse suspension) techniques contained approximately 57 parts per million acrylic acid. In the presence of 2 of the surfactant alone, these levels were only marginally reduced. In the presence of sodium bisulfite alone or admixtures of sodium bisulfite with 2 preferred surfactants, essentially the same results were obtained, all results being less than 10 parts per million residual acrylic acid. Again, it was felt that the initial amount of sodium bisultite was too high to demonstrate the effect of the combination of this invention. The data in Table VI was then generated.

TABLE VI

SAMPLE 3324-	%SBS	%SBS SOL	SURFACTANT 0.11 %	DI H_2O(G)	DRY POWDER (G)	RESIDUAL AA(PPM)
14A	--	--	--	133	125	43
14B	0.29	0.27	--	133	125	9.5
14C	0.29	0.27	Sodium lauryl sulfate	133	125	7.0
14D	0.29	0.27	Surf. EO-ALC	133	125	4

Again, in Table VI a dry powder superabsorbent was obtained from inverse suspension polymerization, which dry powder contained 43 parts per million residual acrylic acid. Treatment with sodium bisulfite alon at considerably lower concentrations than previously tried permitted lowering this residual acrylic acid to about 9.5 parts per million. However, treatment at this level of sodium bisultite in combination with sodium lauryl sulfate or with an ethylen oxide based surfactant demonstrated residual acrylic acid at concentrations ranging from 4 to about 7 parts per million.

The analytical technique is effective in its ability to determine the absolute amount of residual acrylic acid at these concentrations, and comfort is taken in the fact that we hav demonstrated, by the numerical results

obtained, that the combination does provide a better result than does sodium bisulfite alone.

As earlier taught, there are alternative vinylic addition compounds other than sodium bisulfite. To demonstrate the effectiveness of these compounds by themselves, the results in Table VII were generated.

TABLE VII

SAMPLE 3324	TREATMENT	%TREATMENT BOPW	%SOL BOT	COMMERCIAL DRY POWDER (G)	RESIDUAL AA (PPM)
Control	--	--	--	--	300
6A	Aminoiminomethanesulfinic Acid	3	2.5	250	26
6B	Sodium hypophosphite	3	2.5	250	230
6C	Sodium hypophosphite,	3	2.5	250	117
	Ammonium persulfate	0.5	2.0		

Table VII shows the ability of certain of these vinylic addition compounds to reduce residual acrylic acid in the absence of surfactant. It is believed and expected that in the presence of the surfactants defined herein and as outlined in prior tables, additional improvement would be seen in achieving lowered monomer residuals. The results would be expected to be comparable to those shown with the SBS-surfactant combinations.

In summary, we have demonstrated a process for decreasing the residual (meth)acrylic acid monomer content of superabsorbent polymers to levels below about approximately 50 and preferably below about 10 parts per million, based on dry polymer, which process comprises adding to an aqueous superabsorbent polymer gel, or a dried gel obtained therefrom, a combination of a surfactant and a chemical compound capable of vinylic addition or reaction with across a vinylic double bond, where the surfactant and chemical addition compound are contained in combination at a weight ratio ranging from 50:50 to 0.1:99.9 and the combination is added to the superabsorbent polymer at either the superabsorbent gel stages prior to drying or to the dried superabsorbent polymer gel at concentrations of active total combination product (normally added as a water solution) ranging at least from 0.05 weight percent (based on dry polymer) to as much as 10 weight percent, based on dry polymer, or above, admixing, reacting, and drying the so threated superabsorbent polymer, either as a gel, a chopped gel, an emulsion polymer bead, or a dry product, to obtain a superabsorbent dry polymer containing less than 50, and preferably less than 10 parts per million residual (meth)acrylic acid or its salts.

The surfactant used in the combination product preferably has an HLB ranging from about 3 to about 40, preferably from about 8 - 40, and most preferably from about 12 - 40, and is capable of lowering the surface tension of pure water to between about 15 to about 50 dynes/cm when added to water at least l00 - 1,000 parts per million, or above.

We have also taught a composition of superabsorbent polymer, which polymer is manufactured from (meth)acrylic acid, or alkali metal salts thereof, or mixtures thereof, in the presence of di- or tri-vinylic/allylic cross-linking agents, and contains residual (meth)acrylic monomers content below 50, and preferably below 10 parts per million, based on dry polymer weight. The low residual monomer superabsorbent polymer is manufactured by any process which obtains a wet superabsorbent polymer gel, either as an aqueous gel or finally divided aqueous gels, or as finely dispersed water gel bead in a continuous oil phase. However obtained, the water gel is then treated with admixtures of our surfactants and vinylic addition compounds, thereby forming a treated gel, which, on reacting and drying, obtains a dry superabsorbent polymer containing l ss than 50 and preferably less than 10 parts per million residual (m th)acrylic acid monomer.

To the best of our knowledge, this is the first time that anyone has been able to consistently achieve a superabsorbent polymer which contains residual acrylic acid or (meth)acrylic acid monom r below 10 parts per million, based on dry polymer weight. The techniques f combining a surfactant and a vinyl addition compound

for this purpose are not taught in the art, and the description of the invention above clearly shows unexpected results in terms of the use of the combination.

Claims

1. A method for reducing residual (meth)acrylic acid present in water insoluble polyacrylic acid water absorbent gel polymers which comprises treating these polymers, either as a water gel, a water gel dispersed in oil, or as a dry polymer with at least 0.05 weight percent, based on dry polymer of a combination of a surfactant and a vinylic addition compound.

2. The method according to claim 1 wherein the surfactant has an HLB ranging from 3 to 40 and is capable, when added to pure water at a concentration of at least 1000 ppm, of lowering the water surface tension to between 15 to 50 dynes/cm at standard temperature and pressure.

3. The method of claim 2 wherein the surfactant has an HLB ranging from about 8 to about 40.

4. The method of claim 3 wherein the surfactant has an HLB ranging from about 12 to about 40.

5. The method of any preceding claim wherein the vinylic addition compound is one or more of:
   a. sulfites, or alkali metal salts thereof,
   b. bisulfites, or alkali metal salts thereof,
   c. phosphites, or alkali metal salts thereof,
   d. hypophosphites, or alkali metal salts thereof,
   e. alkyl or aromatic sulfinic, or substituted alkyl or aryl sulfinic acids, or salts thereof,
   f. cysteine,
   g. lysine,
   h. biphosphites, or alkali metal salts thereof; and further wherein the combination contains, on a neat basis, a weight ratio of surfactant to vinylic addition compound ranging from about 50:50 to about 0.1 to 99.9.

6. The method according to claim 1 wherein the surfactant is one of:
   a. methoxy terminated ethylene oxide adducts of siloxane,
   b. 4-24 mole ethylene oxide adducts of C_{12}-C_{14} fatty alcohols,
   c. ethylene oxide or propylene oxide adducts of glycerin or glycol,
   d. C_{10} - C_{30} fatty acid sulfonates, and their alkali metal salts,
   e. C_{10} - C_{30} fatty acids, and their alkali metal salts,
   and the so treated polymer is dried at a temperature of at least 180°F.

7. The method of claims 1 or 2 wherein the surfactant is one of sodium lauryl sulfate, ethoxylated polydimethyl siloxane - methoxy capped, ethoxylated (6-12 mole) C_{12} - C_{14} fatty alcohols, glycerin initiated ethylene oxide-propylene oxide adducts, or potassium stearate.

8. The method according to claim 7 wherein the vinylic addition compound is sodium bisulfite.

9. The method according to claim 7 wherein the vinylic addition compound is aminoiminomethanesulfinic acid.

10. The method according to claim 7 wherein the vinylic addition compound is an alkali metal salt of hypophosphite.

11. The method according to any preceding claim wherein, in addition to the combination of surfactant and vinylic addition compound, a salt of an oxidizing anion is also added.

12. The method according to claim 11 wherein the salt of an oxidizing anion is one or more of alkali metal or ammonium salts of persulfate anions.

13. A process for decreasing the residual (meth)acrylic acid monomer content of superabsorbent polymers to levels below about 10 parts per milli n, on the basis of dry polymer, which process comprises adding to an aqu ous superabsorb nt polymer g l, prior to drying, a combination of:

(a) a surfactant, and
(b) a chemical compound capable of adding across a vinylic carbon to carbon bond
wherein the weight ratio of (a):(b) ranges from 50:50 to 0.1 to 99.9, and the combination is added to the aqueous superabsorbent polymer gel at concentrations of the total combination of at least 0.05 weight percent, based on dry polymer; and then drying the aqueous superabsorbent polymer gel.

14. The process according to claim 1 wherein the surfactant has an HLB ranging from about 3 to about 40 and is capable, when added to pure water at a concentration of at least 1000 ppm, of lowering the surface tension of pure water to between about 15 to about 50 dynes/cm, at standard temperatures and pressure.

15. The process according to claim 11 or claim 14 wherein the surfactant is one or more of methoxy terminated ethylene oxide adducts of siloxane, 4-24 mole ethylene oxide adducts of C_{12} - C_{14} fatty alcohols, ethylene oxide/propylene oxide adducts of glycol, glycerin, alkali metal salts of fatty acids having from 10 to about 30 carbon atoms, or mixtures thereof; alkali metal salts of fatty acid sulfates containing from 10 - 30 carbon atoms.

16. The process according to claim 13 wherein the chemical compound capable of adding across a vinylic bond is one or more of alkali metal salts of sulfites, bisulphites, their anhydrides or mixtures thereof; alkyl or aryl, or substituted alkyl or aryl sulfinic acids, or water soluble salts thereof; alkali metal salts of thiosulfates alkali metal salts of hypophosphites; sulfur containing amino acids, or water soluble salts thereof.

17. The process according to claim 16 wherein the chemical compound capable of adding across a vinylic bond is one or more of:
a. sodium or potassium sulfite;
b. sodium or potassium bisulfites;
c. aminoiminomethanesulfinic acid, or salts thereof;
d. alkali metal salts or hypophophites;
e. alkali metal salts of thiosulfates;
f. cysteine;
g. lysine.

18. A superabsorbent polymer containing (meth)acrylic acid, or alkali metal salts thereof, a di- or trivinylic/allylic cross-linking agent, and a residual (meth)acrylic acid monomer content below 10 ppm, based on dry polymer weight, which superabsorbent polymer is manufactured by a process which obtains a wet superabsorbent polymer gel, either as a gel or as a finely dispersed water gel in a continuous oil phase, which water gel is then treated with an admixture of:
a. a surfactant, and
b. a compound capable of addition across a vinylic double bond,
thereby forming a treated gel; and then drying said treated gel to obtain a dry superabsorbent polymer containing less than 10 ppm residual (meth)acrylic acid monomer.

19. The superabsorbent polymer of claim 18 wherein the surfactant has an HLB of between about 3 and about 40 and is capable when added to pure water at a concentration of at least 1000 ppm of lowering the pure water surface tension to from about 15 to about 50 dynes/cm; and the compound capable of promoting addition across a vinylic double bond is one or more of:
a. alkali metal sulfites;
b. alkali metal bisulfites;
c. alkyl or aryl, or substituted alkyl or aryl sulfinic acids, or salts thereof;
d. hypophosphites, and salts thereof;
e. sulfur containing amino acids, and salts thereof; and further wherein the admixture ratio of a:b ranges from 50:50 to 0.1:99.9.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92302328.7

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP - A - 0 441 975 (NIPPON SHOKUBAI KAGAKU) * Claims 1,8-13,20-22,24 * --	1-5, 13,14, 16-18	C 08 F 6/00 A 61 L 15/24
D,A	US - A - 4 929 717 (CHMELIR) * Claims 1,2; column 2, line 60 - column 3, line 13 * --	1,5,8, 13,16, 17	
D,A	US - A - 4 766 173 (BAILEY et al.) * Claims 1-3 * ----	1,5, 13,16, 17	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

A 61 L 15/00
C 08 F 6/00
C 08 F 20/00
C 08 F 220/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	16-06-1992	PUSTERER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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